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VERIFICATION OF A TRANSLATION

I, Susan ANTHONY BA, ACIS,

Director of RWS Group Ltd, of Europa House, Marsham Way, Gerrards Cross, Buckinghamshire, England declare:

That the translator responsible for the attached translation is knowledgeable in the German language in which the below identified international application was filed, and that, to the best of RWS Group Ltd knowledge and belief, the English translation of the international application No. PCT/EP03/06176 is a true and complete translation of the above identified international application as filed.

I hereby declare that all the statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the patent application issued thereon.

Date: November 24, 2004

Signature :



For and on behalf of RWS Group Ltd

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England.

Process for curing amino resins

The invention relates to a process for curing amino resins and also to amino resin products produced by the process.

Amino resins such as melamine-formaldehyde resins or melamine-urea-formaldehyde resins [Ullmann's Encyclopaedia of Industrial Chemistry (1987), vol. A2, 130-131] are known. A disadvantage associated with the production of products from melamine resins is the difficulty of processing them by customary thermoplastic processing methods such as extrusion, injection molding or blow molding. Low molecular mass melamine resin precondensates have a melt viscosity which is too low for these processing methods, and can be processed only in the form of highly filled molding compounds with long cycle times and with curing of the products (Woebcken, W., Kunststoff-Handbuch vol. 10, "Duroplaste" [Thermosets], Carl Hanser Verlag Munich 1988, pp. 266-274).

Fibres [DE 195 15 277 A1, EP 0 093 965 A2], foams or coatings [DE 24 22 803 B1] of melamine resins can be produced only starting from solutions of the melamine resin precondensates, with curing during the shaping operation, owing to the low melt viscosity of the melamine resin precondensates.

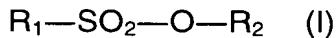
Known curing agents in the production of melamine resin fibres are organic acids such as formic acid, acetic acid, amidosulphonic acids or amino acids [DE 195 15 277 A1] or alkali metal salts such as alkali metal disulphides, alkali metal phosphates or alkali metal polyphosphates [EP 0 093 965 A2].

Also known is the use of iodonium salts (DE 100 63 066) or of blocked sulphonic acids (WO 00 10 972) as a component of radiation-sensitive polymerizable or crosslinkable formulations.

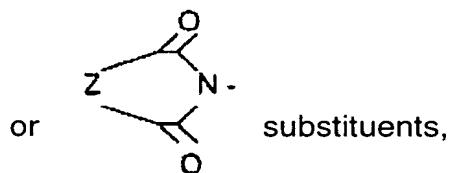
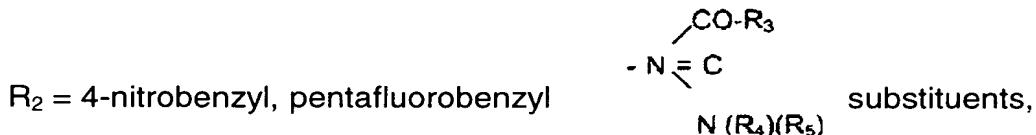
An object of the present invention is a process for curing amino resins with which solvent-free thin amino resin layers or amino resin filaments can be cured.

The object has been achieved by a process for curing amino resins in which, in accordance with the invention, layers with thicknesses up to 300 µm or filaments or fibrids with a diameter up to 300 µm and composed of

- a) from 95 to 99.95% by mass of solvent-free meltable amino resin polycondensates having molar masses of 300 to 300 000,
- b) from 5 to 0.05% by mass of curing agents which can be activated by actinic light and are composed of
  - b1) acid formers of the type of blocked sulphonic acid of the general formula (I)



$R_1$  = unsubstituted or substituted aryl, biphenyl or alkyl,



$Z$  = C<sub>6</sub>-C<sub>24</sub>-aryl, C<sub>2</sub>-C<sub>4</sub>-alkyl, C<sub>2</sub>-C<sub>4</sub>-alkenyl,  
C<sub>7</sub>-C<sub>8</sub>-bicycloalkenyl,

where  $R_3$  = non-substituted or substituted alkyl or aryl,

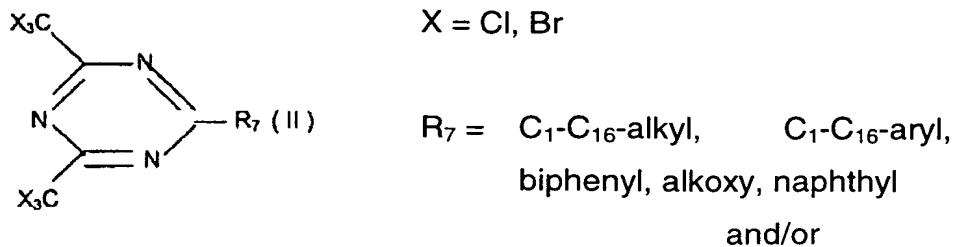
$R_4$  = H, C<sub>1</sub>-C<sub>12</sub>-alkyl, phenyl, C<sub>2</sub>-C<sub>9</sub>-alkanoyl or benzyl,

$R_5$  = H, C<sub>1</sub>-C<sub>12</sub>-alkyl or cyclohexyl

or  $R_3$  and  $R_4$  or  $R_5$  together with the atoms to which they attached form a 5- to 8-membered ring which can be fused by 1 or 2 benzo radicals,

and/or

b2) halogen-substituted triazine derivatives of the general formula (II)



b3) onium salts of the type of aryl diazonium salts, diarylhalonium salts, triarylsulphonium salts, triarylselenonium salts and/or N-alkoxypyridinium salts,

and if desired

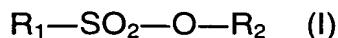
- c) from 1 to 20% by mass, based on the meltable amino resin polycondensates, of non-modified and/or modified maleic anhydride copolymers, and/or
- d) from 0.1 to 5% by mass, based on the meltable amino resin polycondensates, of nanoparticles in the form of phyllosilicates, hydrophilic or hydrophobic synthetic silicas, calcium carbonate or metal oxides of the ZnO, SnO, Al<sub>2</sub>O<sub>3</sub> or TiO<sub>2</sub> type.

are cured by irradiation with actinic light at a temperature between the melting point of the amino resin polycondensate and the thermoinduced decomposition temperature of the light-activable curing agents, and if desired are subjected to a thermal aftercure below 250°C.

Suitable light sources are point light sources and panel-form emitters. Examples of suitable light sources are carbon arc lamps, xenon arc lamps, mercury emitters in the low pressure, medium pressure and high pressure range, which may where appropriate have been doped with metal halides, such as metal-halogen lamps, microwave-excited metal vapour lamps, excimer lamps, superactinic fluorescent tubes, fluorescent lamps, argon incandescent lamps, flash lamps, and laser light sources

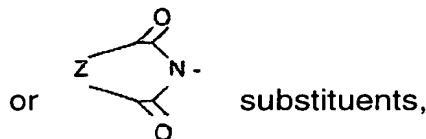
such as excimer lasers.

In the process for curing amino resins preferred acid formers of the type of blocked sulphonic acid of the general formula



are blocked sulphonic acids in which the substituents

$R_1$  = unsubstituted or singly or multiply halogen-,  $C_1-C_4$ -haloalkyl-,  $C_1-C_{16}$ -alkyl-,  $C_1-C_4$ -alkoxy-,  $C_1-C_4$ -alkyl-CO-NH-, phenyl-CO-NH-, benzoyl- and/or nitro-substituted  $C_6-C_{10}$ -aryl or  $C_7-C_{12}$ -arylalkyl,



$Z$  =  $C_6-C_{24}$ -aryl,  $C_2-C_4$ -alkyl,  $C_2-C_4$ -alkenyl,  $C_7-C_8$ -bicycloalkenyl,

where

$R_3$  =  $C_1-C_{12}$ -alkyl,  $C_1-C_4$ -haloalkyl,  $C_2-C_6$ -alkenyl,  $C_5-C_{12}$ -cycloalkyl, unsubstituted or singly or multiply halogen-,  $C_1-C_4$ -haloalkyl-,  $C_1-C_{16}$ -alkyl-,  $C_1-C_4$ -alkoxy-,  $C_1-C_4$ -alkyl-CO-NH-, phenyl-CO-NH-, benzoyl- and/or nitro-substituted  $C_6-C_{10}$ -aryl and/or  $C_7-C_{12}$ -arylalkyl,  $C_1-C_8$ -alkoxy,  $C_5-C_8$ -cycloalkoxy, phenoxy or  $H_2N-CO-NH-$ ,  $-CN$ ,  $C_2-C_5$ -alkyloyl, benzoyl,  $C_2-C_5$ -alkoxycarbonyl, phenoxy carbonyl, morpholino, piperidino,  $C_1-C_{12}$ -alkyl,  $C_1-C_4$ -haloalkyl,  $C_2-C_6$ -alkenyl,  $C_5-C_{12}$ -cycloalkyl, unsubstituted or singly or multiply halogen-,  $C_1-C_4$ -haloalkyl-,  $C_1-C_{16}$ -alkyl,  $C_1-C_4$ -alkoxy,  $C_1-C_4$ -alkyl-CO-NH-, phenyl-CO-NH-, benzoyl- and/or nitro-substituted  $C_6-C_{10}$ -aryl,  $C_7-C_{12}$ -arylalkyl,  $C_1-C_8$ -alkoxy,  $C_5-C_8$ -cycloalkoxy-, phenoxy- or  $H_2N-CO-NH-$ ,

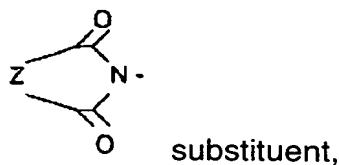
$R_4$  = H, C<sub>1</sub>-C<sub>12</sub>-alkyl, phenyl, C<sub>2</sub>-C<sub>9</sub>-alkanoyl or benzyl

$R_5$  = H, C<sub>1</sub>-C<sub>12</sub>-alkyl or cyclohexyl,

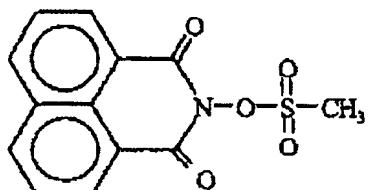
or  $R_3$  and  $R_4$  or  $R_5$  together with the atoms to which they are attached form a 5- to 8-membered ring which can be fused by 1 or 2 benzo radicals.

Examples of preferred blocked sulphonic acids are benzil monoxime tosylate, benzil monoxime p-dodecylbenzenesulphonate, 4-nitroacetophenone oxime tosylate, ethyl  $\alpha$ -tosyloximinocaproate, ethyl  $\alpha$ -cyclohexylsulphonyloxyiminophenylacetate, phenyl  $\alpha$ -(4-chlorophenylsulphonyloxyimino)caproate, 4,4-dimethylbenzil monoxime tosylate, dibenzyl ketone oxime tosylate, acetone oxime p-benzoylbenzenesulphonate,  $\alpha$ -tretralone oxime tosylate, anthraquinone monoxime tosylate, thioxanthone oxime tosylate,  $\alpha$ -(p-toluenesulphonyloxyimino)benzyl cyanide,  $\alpha$ -(4-nitrobenzenesulphonyloxyimino)benzyl cyanide,  $\alpha$ -(benzenesulphonyloxyimino)-4-chlorobenzyl cyanide,  $\alpha$ -(benzenesulphonyloxyimino)-2,6-dichlorobenzyl cyanide,  $\alpha$ -(2-chlorobenzenesulphonyloxyimino)-4-methoxybenzyl cyanide, 4-chloro- $\alpha$ -trifluoroacetophenone oxime benzenesulphonate, fluorene oxime tosylate,  $\alpha$ -(benzenesulphonyloxyimino)ureidocarbonylacetonitrile,  $\alpha$ -(p-toluenesulphonyloxyimino)benzoylacetonitrile, 2,3-dihydro-1,4-naphthoquinone monoxime tosylate, acetophenone oxime tosylate, chroman oxime tosylate, 2-nitrobenzyl sulphonate, 2,6-dinitrobenzyl benzenesulphonate, 4-nitrobenzyl 9,10-dimethoxyanthracene-2-sulphonate, 2-methylsulphonyloxyimino-4-phenylbut-3-enenitrile, 4-cyclohex-1-enyl-2-methylsulphonyloxyiminobut-3-enenitrile, 4-furan-2-ylisopropylsulphonyloxyiminobut-3-enenitrile and 2-pentafluorophenylsulphonyloxyimino-4-phenylbut-3-enenitrile.

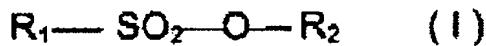
One example of preferred blocked sulphonic acids in which  $R_2$  is an



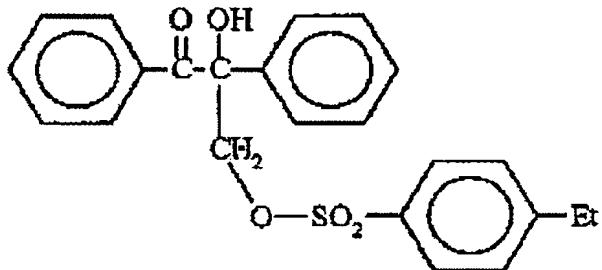
is the blocked sulphonic acid of the structure



Particular preference is given in the process of the invention for curing amino resins to acid formers of the type of blocked sulphonic acid of the general formula

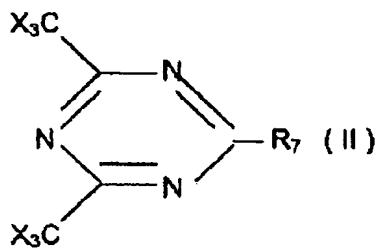


in which the blocked sulphonic acids are acid formers of the formula



Examples of halogen-substituted triazine derivatives which can be used in the process of the invention as curing agents which can be activated by actinic light are 1,3,5-tribromomethyl-2,4,6-triazine and 1,3,5-trichloromethyl-2,4,6-triazine.

In the process of the invention for curing amino resins preferred halogen-substituted triazine derivatives of the general formula (II)



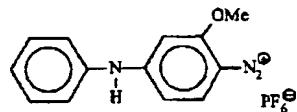
are triazine derivatives in which

$X = Cl$  and  $R_7 = p$ -methoxyphenyl.

Examples of onium salts which can be used in the process of the invention as curing agents which can be activated by actinic light are

- aryl diazonium salts such as phenyldiazonium hexafluoroarsenate, tolyldiazonium tetrafluoroborate and phenyldiazonium hexafluorophosphate,
- diarylhalonium salts such as 4-isobutylphenyl-4'-methylphenyliodonium hexafluorophosphate, 4-isobutylphenyl-4'-methylphenyliodonium 4-chlorophenylsulphonate, 4-(menthylbut-2-yl)phenyl-4'-methylphenyliodonium nonafluorobutylsulphonate, diphenylbromonium hexafluoroantimonate, diphenyliodonium 8-anilinonaphthaline-1-sulphonate, diphenyliodonium 9,10-dimethoxyanthracene-2-sulphonate and diphenylchloronium hexafluoroantimonate,
- triarylsulphonium salts such as tris(4-methoxyphenyl)sulphonium hexafluoroarsenate, 3,5-dimethyl-4-hydroxyphenylsulphonium hexafluorophosphate and benzyl(p-hydroxyphenyl)methylsulphonium hexafluoroantimonate,
- triarylselenonium salts such as 3,5-diphenyl-4-hydroxyphenylsulfonium tetrafluoroborate and tris(4-ethoxyphenyl)sulfonium hexafluorophosphate,
- N-alkoxypyridinium salts such as N-ethoxypyridinium tetrafluoroborate or N-methoxypyridinium hexafluorophosphate.

A preferred onium salt curing agent is the onium salt of the formula



The amino resin polycondensates with molar masses of 1000 to 300 000 that are used in the process of the invention to cure amino resins are preferably polycondensates of melamine resins, urea resins, cyanamide resins, dicyandiamide resins, sulphonamide resins and/or guanamine resins.

Preferred melamine resins are polycondensates of melamine and/or melamine derivatives and C<sub>1</sub>-C<sub>8</sub> aldehydes having a melamine or melamine derivative/C<sub>1</sub>-C<sub>8</sub> aldehyde molar ratio of 1:1.5 to 1:6 and also their partial etherification products, it being possible for the melamine derivatives to be melamines substituted by hydroxy-C<sub>1</sub>-C<sub>10</sub>-alkyl groups, hydroxy-C<sub>1</sub>-C<sub>4</sub>-alkyl(oxa-C<sub>2</sub>-C<sub>4</sub>-alkyl)<sub>1-5</sub> groups and/or by amino-C<sub>1</sub>-C<sub>12</sub>-alkyl groups, ammeline, ammelide, melem, melon, melam, benzoguanamine, acetoguanamine, tetramethoxymethylbenzoguanamine, caprinoguanamine and/or butyroguanamine, and the C<sub>1</sub>-C<sub>8</sub> aldehydes are, in particular, formaldehyde, acetaldehyde, trimethylolacetaldehyde, acrolein, furfural, glyoxal and/or glutaraldehyde, with particular preference formaldehyde.

The melamine resins may likewise contain 0.1 to 10% by mass, based on the sum of melamine and melamine derivatives, of incorporated phenols and/or urea. Suitable phenol components include phenol, C<sub>1</sub>-C<sub>9</sub>-alkylphenols, hydroxyphenols and/or bisphenols.

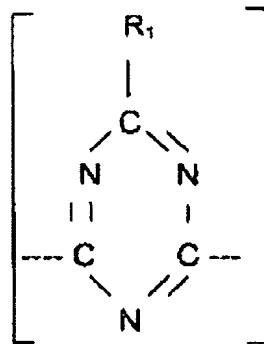
Examples of the urea resins possibly employed in the process of the invention, besides urea-formaldehyde resins, likewise include cocondensates with phenols, acid amides or sulphonamides.

Examples of the sulphonamide resins possibly employed in the process of the invention are sulphonamide resins formed from p-toluenesulphonamide and formaldehyde.

Examples of the guanamine resins possibly employed in the process of the invention are resins comprising as guanamine component benzoguanamine, acetoguanamine, tetramethoxymethylbenzoguanamine, caprinoguanamine and/or butyroguanamine.

Examples of the aniline resins possibly employed in the process of the invention are aniline resins which as aromatic diamines may contain, as well as aniline, toluidine and/or xylydines.

With particular advantage the process of the invention for curing amino resins uses polycondensates of melamine resins that are mixtures of meltable 4- to 1000-nucleus polytriazine ethers, where in the polytriazine ethers the triazine segments



$R_1 = -NH_2, -NH-CHR_2-O-R_3, -NH-CHR_2-O-R_4-OH, -CH_3, -C_3H_7, -C_6H_5, -OH, phthalimido-, succinimido-, -NH-CO-C_5-C_{18}-alkyl, -NH-C_5-C_{18}-alkylene-OH, -NH-CHR_2-O-C_5-C_{18}-alkylene-NH_2, -NH-C_5-C_{18}-alkylene-NH_2, -NH-CHR_2-O-R_4-O-CHR_2-NH-, -NH-CHR_2-NH-, -NH-CHR_2-O-C_5-C_{18}-alkylene-NH-, -NH-C_5-C_{18}-alkylene-NH-, -NH-CHR_2-O-CHR_2-NH-,$

$R_2 = H, C_1-H_7-alkyl;$

$R_3 = C_1-C_{18}-alkyl, H;$

$R_4 = C_2\text{-}C_{18}\text{-alkylene}$ ,

- $CH(CH_3)\text{-}CH_2\text{-}O\text{-}C_2\text{-}C_{12}\text{-alkylene-O-}CH_2\text{-}CH(CH_3)\text{-}$ ,

- $CH(CH_3)\text{-}CH_2\text{-}O\text{-}C_2\text{-}C_{12}\text{-arylene-O-}CH_2\text{-}CH(CH_3)\text{-}$ ,

- $[CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2]_n\text{-}$ , - $[CH_2\text{-}CH(CH_3)\text{-}O\text{-}CH_2\text{-}CH(CH_3)]_n\text{-}$ ,

- $[-O\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2]_n\text{-}$ ,

- $[(CH_2)_{2-8}\text{-}O\text{-}CO\text{-}C_6\text{-}C_{14}\text{-arylene-CO-O-(CH_2)_{2-8}\text{-}}]_n\text{-}$ ,

- $[(CH_2)_{2-8}\text{-}O\text{-}CO\text{-}C_2\text{-}C_{12}\text{-alkylene-CO-O-(CH_2)_{2-8}\text{-}}]_n\text{-}$ ,

where  $n = 1$  to 200;

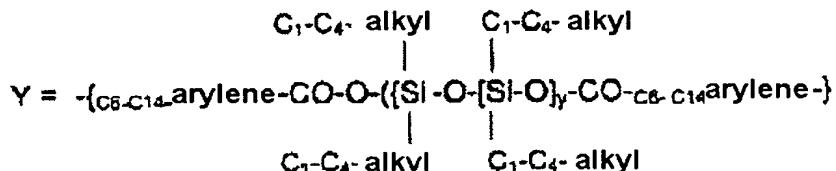
- polyester sequences containing siloxane groups, of the type

- $[(X)_r\text{-}O\text{-}CO\text{-}(Y)_s\text{-}CO\text{-}O\text{-}(X)_r\text{-}]$

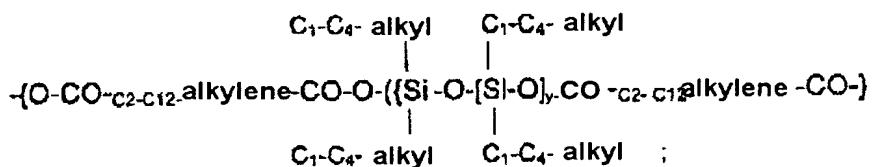
in which

$X = \{(CH_2)_{2-8}\text{-}O\text{-}CO\text{-}C_8\text{-}C_{14}\text{-arylene-CO-O-(CH_2)_{2-8}\text{-}}\}$  or

$\{(CH_2)_{2-8}\text{-}O\text{-}CO\text{-}C_2\text{-}C_{12}\text{-alkylene-CO-O-(CH_2)_{2-8}\text{-}}\}$

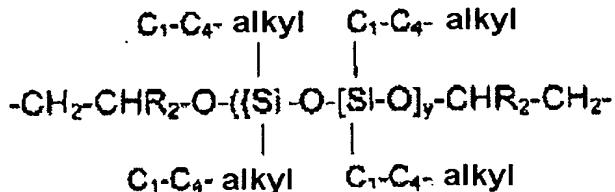


or



$r = 1$  to 70;  $s = 1$  to 70 and  $y = 3$  to 50;

- polyether sequences containing siloxane groups, of the type



where  $R_2 = H$ ;  $C_1\text{-}C_4\text{-alkyl}$  and  $y = 3$  to 50;

- sequences based on alkylene oxide adducts of melamine, of the type

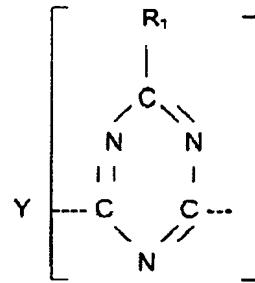
of 2-amino-4,6-di- $C_2\text{-}C_4$ -alkylenamino-1,3,5-triazine sequences;

- phenol ether sequences based on dihydric phenols and C<sub>2</sub>-C<sub>8</sub> diols of the type of -C<sub>2</sub>-C<sub>8</sub>-alkylene-O-C<sub>6</sub>-C<sub>18</sub>-arylene-O-C<sub>2</sub>-C<sub>8</sub>-alkylene-sequences;

are linked by bridge members -NH-CHR<sub>2</sub>-NH- or -NH-CHR<sub>2</sub>-O-R<sub>4</sub>-O-CHR<sub>2</sub>-NH- and -NH-CHR<sub>2</sub>-NH- and also, where appropriate, -NH-CHR<sub>2</sub>-O-CHR<sub>2</sub>-NH-, -NH-CHR<sub>2</sub>-O-C<sub>5</sub>-C<sub>18</sub>-alkylene-NH- and/or -NH-C<sub>5</sub>-C<sub>18</sub>-alkylene-NH- to form 4- to 1000-nucleus polytriazine ethers with a linear and/or branched structure,

where in the polytriazine ethers the molar ratio of the substituents R<sub>3</sub>:R<sub>4</sub> = 20:1 to 1:20 and the fraction of the linkages of the triazine segments through bridge members -NH-CHR<sub>3</sub>-O-R<sub>4</sub>-O-CHR<sub>3</sub>-NH- is from 5 to 95 mol%.

The terminal triazine segments in the polytriazine ethers are triazine segments of the structure



Y = -NH-CHR<sub>2</sub>-O-R<sub>3</sub>, -NH-CHR<sub>2</sub>-O-R<sub>4</sub>-OH and, if desired, -NH-CHR<sub>2</sub>-O-C<sub>5</sub>-C<sub>18</sub>-alkylene-NH<sub>2</sub>, -NH-C<sub>5</sub>-C<sub>18</sub>-alkylene-NH<sub>2</sub>, -NH-C<sub>5</sub>-C<sub>18</sub>-alkylene-OH,

R<sub>1</sub> = -NH<sub>2</sub>, -NH-CHR<sub>2</sub>-O-R<sub>3</sub>, -NH-CHR<sub>2</sub>-O-R<sub>4</sub>-OH, -CH<sub>3</sub>, -C<sub>3</sub>H<sub>7</sub>, -C<sub>6</sub>H<sub>5</sub>, -OH, phthalimido-, succinimido, -NH-CO-R<sub>3</sub>, -NH-C<sub>5</sub>-C<sub>18</sub>-alkylene-OH, -NH-C<sub>5</sub>-C<sub>18</sub>-alkylene-NH<sub>2</sub>, -NH-CHR<sub>2</sub>-O-C<sub>5</sub>-C<sub>18</sub>-alkylene-NH<sub>2</sub>,

R<sub>2</sub> = H, C<sub>1</sub>-C<sub>7</sub>-alkyl;

R<sub>3</sub> = C<sub>1</sub>-C<sub>18</sub>-alkyl, H;

R<sub>4</sub> = C<sub>2</sub>-C<sub>18</sub>-alkylene,

$-\text{CH}(\text{CH}_3)\text{-CH}_2\text{-O-c}_2\text{-c}_{12}\text{-alkylene-O-CH}_2\text{-CH}(\text{CH}_3)\text{-}$ ,  
 $-\text{CH}(\text{CH}_3)\text{-CH}_2\text{-O-c}_2\text{-c}_{12}\text{-arylene-O-CH}_2\text{-CH}(\text{CH}_3)\text{-}$ ,  
 $-\text{[CH}_2\text{-CH}_2\text{-O-CH}_2\text{-CH}_2\text{]}_n\text{-}$ ,  $-\text{[CH}_2\text{-CH}(\text{CH}_3)\text{-O-CH}_2\text{-CH}(\text{CH}_3)\text{]}_n\text{-}$ ,  
 $-\text{[-O-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{]}_n\text{-}$ ,  
 $-\text{[(CH}_2\text{)}_{2-8}\text{-O-CO-c}_6\text{-c}_{14}\text{-arylene-CO-O-(CH}_2\text{)}_{2-8}\text{]}_n\text{-}$ ,  
 $-\text{[(CH}_2\text{)}_{2-8}\text{-O-CO-c}_2\text{-c}_{12}\text{-alkylene-CO-O-(CH}_2\text{)}_{2-8}\text{]}_n\text{-}$ ,

where  $n = 1$  to 200;

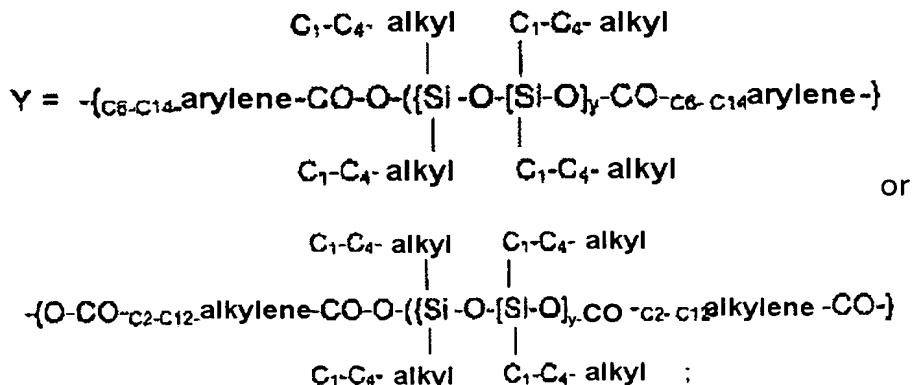
- polyester sequences containing siloxane groups, of the type

$$-[(X)_r-O-CO-(Y)_9-CO-O-(X)_r]-$$

in which

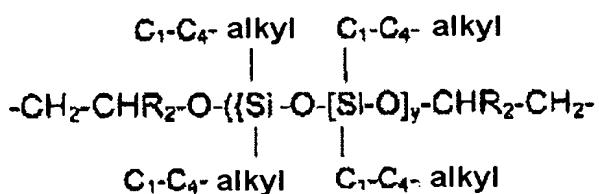
X =  $\{(\text{CH}_2)_{2-8}\text{-O-CO-C}_6\text{-C}_{14}\text{-arylene-CO-O-(CH}_2\text{)}_{2-8}\}$  or

-{(CH<sub>2</sub>)<sub>2-8</sub>-O-CO-C<sub>2</sub>-C<sub>12</sub>-alkylene-CO-O-(CH<sub>2</sub>)<sub>2-8</sub>-}



$r = 1$  to 70;  $s = 1$  to 70 and  $y = 3$  to 50;

- polyether sequences containing siloxane groups, of the type



where  $R_2 = H$ ;  $C_1-C_4$ -alkyl and  $\gamma = 3$  to 50;

- sequences based on alkylene oxide adducts of melamine, of the type of 2-amino-4,6-di- $C_2-C_4$ -alkylenamino-1,3,5-triazine sequences form;

- phenol ether sequences based on dihydric phenols and C<sub>2</sub>-C<sub>8</sub> diols of the type of -C<sub>2</sub>-C<sub>8</sub>-alkylene-O-C<sub>6</sub>-C<sub>18</sub>-arylene-O-C<sub>2</sub>-C<sub>8</sub>-alkylene-sequences.

The 4- to 1000 nucleus polytriazine ethers used in the process of the invention can be prepared by etherifying melamine resin precondensates with C<sub>1</sub>-C<sub>4</sub> alcohols, where appropriate with subsequent partial transesterification with C<sub>4</sub>-C<sub>18</sub> alcohols, C<sub>2</sub>-C<sub>18</sub> diols, polyhydric alcohols of the glycerol or pentaerythritol type, C<sub>5</sub>-C<sub>18</sub> amino alcohols, polyalkylene glycols, polyesters containing hydroxyl end groups, siloxane polyesters, siloxane polyethers, melamine-alkylene oxide adducts and/or binuclear-phenol-alkylene oxide adducts and/or reaction with C<sub>5</sub>-C<sub>18</sub> diamines and/or bisepoxides, and subsequent thermal condensation of the modified melamine resin condensates in the melt in a continuous compounder at temperatures of 140 to 220°C.

Examples of maleic anhydride copolymers used where appropriate in the process of the invention are C<sub>2</sub>-C<sub>20</sub> olefin-maleic anhydride copolymers or copolymers of maleic anhydride and C<sub>8</sub>-C<sub>20</sub> vinylaromatics.

Examples of the C<sub>2</sub>-C<sub>20</sub> olefin components which may be present in the maleic anhydride copolymers are ethylene, propylene, but-1-ene, isobutene, diisobutene, hex-1-ene, oct-1-ene, hept-1-ene, pent-1-ene, 3-methylbut-1-ene, 4-methylpent-1-ene, methylethylpent-1-ene, ethylpent-1-ene, ethylhex-1-ene, octadec-1-ene and 5,6-dimethylnorbornene.

Examples of the C<sub>8</sub>-C<sub>20</sub> vinylaromatic components which may be present in the maleic anhydride copolymers are styrene,  $\alpha$ -methylstyrene, dimethylstyrene, isopropenylstyrene, p-methylstyrene and vinylbiphenyl.

Examples of the modified maleic anhydride copolymers used where appropriate in the process of the invention are partially or fully esterified, amidated and/or imidated maleic anhydride copolymers.

Particular suitability is possessed by modified copolymers of maleic anhydride and C<sub>2</sub>-C<sub>20</sub> olefins and/or C<sub>8</sub>-C<sub>20</sub> vinylaromatics with a molar ratio of 1:1 to 1:9 and molar mass weight averages of 5000 to 500 000 that have been reacted with ammonia, C<sub>1</sub>-C<sub>18</sub>-monoalkylamines, C<sub>6</sub>-C<sub>18</sub> aromatic monoamines, C<sub>2</sub>-C<sub>18</sub> monoamino alcohols, monoaminated poly(C<sub>2</sub>-C<sub>4</sub>-alkylene) oxides with a molar mass of 400 to 3000, and/or monoetherified poly(C<sub>2</sub>-C<sub>4</sub>-alkylene) oxides with a molar mass of 100 to 10 000, the molar ration of anhydride groups of copolymer to ammonia, amino groups of C<sub>1</sub>-C<sub>18</sub>-monoalkylamines, C<sub>6</sub>-C<sub>18</sub> aromatic monoamines, C<sub>2</sub>-C<sub>18</sub> monoamino alcohols and/or monoaminated poly(C<sub>2</sub>-C<sub>4</sub>-alkylene) oxide and/or hydroxyl groups of poly(C<sub>2</sub>-C<sub>4</sub>-alkylene) oxide being 1:1 to 20:1.

Examples of the nanoparticles used where appropriate in the process of the invention, in the form of phyllosilicates, are montmorillonite, bentonite, kaolinite, muscovite, hectorite, fluorohectorite, kanemite, revdite, grumantite, ilerite, saponite, beidelite, nontronite, stevensite, laponite, taneolite, vermiculite, halloysite, volkonskoite, magadite, rectorite, kenyaite, sauconite, boron fluorophlogopites and synthetic smectites.

In the process of the invention the meltable amino resin polycondensates containing, where appropriate, maleic anhydride copolymers and/or nanoparticles are used preferably in the form of cylindrical, lenticular, lozenge-shaped or spherical particles having an average diameter of 0.5 to 8 mm in the preparation of the amino resin melts.

Suitable for preparing the melts of the amino resin polycondensates prior to the application of the actinic radiation are continuous compounders, preferably extruders having short compression screws or three-section screws with L/D = 20-40. Preference is given to 5-section screws with an intake section, compression section, shearing section, decompression section and homogenizing section. Screws with depths of cut of 1:2.5 to 1:3.5 are preferentially suitable.

Particularly favourable is the interposition of static mixers or melt pumps between barrel and die.

Maleic anhydride copolymers and/or nanoparticles, where these components have not been incorporated during the actual readying of the amino resin polycondensates, can likewise be added in the continuous compounder to the melt of the amino resin polycondensates.

The temperatures of processing from the melt of the amino resin polycondensates containing light-activable curing agents are determined by the temperature interval above the melting point of the amino resin polycondensates and below the thermoinduced decomposition temperature of the light-activable curing agents.

For an amino resin polycondensate it is advantageous to use a light-activable curing agent whose thermoinduced decomposition temperature is at least 450 degrees above the melting temperature of the amino resin polycondensate. Customary residence times in the continuous compounder when preparing and homogenizing the melt are 2 to 12 min.

In the process of the invention for curing amino resins, layers of amino resins are preferably cured continuously by irradiating the melt layer of the amino resin polycondensate applied to moving carrier materials.

The application of the amino resin melt to the moving carrier material can take place by means of a slot die or by spraying.

Examples of carrier materials to which the melt layer of the amino resin polycondensate is applied in the course of the process of the invention for the purpose of subsequent curing by irradiation are webs of sheetlike textile structures such as nonwovens and wovens, paper, paperboard or wood veneer, or

sheet material of wood, including plywood, wood chipboard, wood fibreboard or multilayer composite board.

Thin foamed layers on the carrier materials can be produced if the melts of the amino resin polycondensates contain gas-evolving blowing agents such as sodium hydrogencarbonate, azodicarboxamide, citric acid/bicarbonate blowing systems and/or cyanuric trihydrazide, or if volatile hydrocarbons such as pentane, isopentane, propane and/or isobutane, or gases such as nitrogen, argon and/or carbon dioxide, are introduced into the melt before it is discharged, with foaming of the layer taking place as the melt is discharged from the slot die.

In the process of the invention for curing amino resins the curing of filaments or fibrils of amino resins takes place preferably continuously by irradiation of the filaments or fibrils, discharged in the form of a viscous melt, after the fibre-forming operation.

The production of filament yarns by the process of the invention can take place in short spinning units by transferring the amino resin polycondensate melt, containing light-activable curing agents, into the capillary die using a melt pump, extruding the filaments into the blowing shaft while at the same time applying actinic light, and taking off the filaments using high-speed godets and subjecting them to further processing in downstream installations comprising thermal aftercure chamber, drawing apparatus and winders.

Fibrils and nonwovens in accordance with the process of the invention can be produced by the melt-blown process by transferring the amino resin polycondensate melt, containing light-activable curing agents, into the capillary die using a melt pump, extruding the filaments from the capillary die into the blowing shaft, while applying a hot stream of air around the apertures in the capillary die and at the same time carrying out irradiation with actinic light. The stream of air stretches the melted filament

and at the same time divides it into a large number of small individual fibres with diameters of 0.5 to 12  $\mu\text{m}$ . The fibrils deposited on the screen conveyor belt can be processed further to nonwovens by applying thermobonding or needling operations in order to achieve the required strength and dimensional stability.

Further in accordance with the invention are amino resin products, preferably sheetlike textile structures or coatings, produced by the process described above.

Examples of sheetlike textile structures are fire-resistant and heat-protection clothing containing amino resin fibres, fire-resistant ceilings, temperature-stable electrical insulation fabric, filter inserts for hot gases, and felts for paper making machines.

Examples of coatings are amino-resin-coated sheetlike textile structures such as nonwovens and wovens and also amino-resin-coated paper, paperboard or wood veneer, or coated sheet material of wood, including plywood, wood chipboard, wood fibreboard or multilayer composite board.

The invention is illustrated by the following examples:

The exposure unit used for irradiation with actinic light was a Fusion UV system model F600s with 1 600-44 lamp section, lamp output 240 W/cm, 6000 W in total, with microwave-pulsed H lamp (Hg spectrum, principal emissions at 200-320 nm and 365 nm), elliptical reflector geometry and cooling by means of an external fan.

To determine the force required for permanent deformation in the scratching test the surface of the cured resin layer was traversed by a needle whose load is increased from 0 to 40 mN in 10 loading steps. The parameter determined

is the force at which the surface of the cured resin layer is permanently deformed.

**Example 1:**

The melamine resin used is a polycondensate of melamine and formaldehyde with a melamine/formaldehyde ratio of 1:3. The methylol groups of the melamine resin are predominantly etherified by methanol; the methoxy group content of the resin is 20% by mass. The molar mass of the resin is around 2000 g/mol.

The etherified melamine resin is homogenized in the melt at 140°C with 1% by mass, based on the melamine resin, of 2-(4-methoxyphenyl)-4,6-bis(trichloromethyl)-1,3,5-triazine as light-activable curing agent and the liquid melt mixture is applied to the surface of a pinewood sheet (thickness 10 mm) in a layer thickness of 50 µm, using a doctor blade, the sheet having been heated to 140°C beforehand, and the coated sheet is irradiated in the exposure unit. For that purpose the sheet is passed beneath the lamp on a conveyor belt and exposed with an output of 1.4 W/cm<sup>2</sup> with an oxygen concentration of 15% by volume and a temperature of 140°C.

The result is a tack-free, fully cured surface. In the scratch test the surface of the cured resin layer is permanently deformed only when a force of 28 mN is applied. In a comparative experiment on an unirradiated coated sheet under the same experimental conditions the surface of the resin layer undergoes permanent deformation at a force of only 4 mM.

**Example 2:**

Experimental procedure as in Example 1. The light-activable curing agent used is 2% by mass, based on the melamine resin, of 2-(4-methoxyphenyl)-4,6-bis(tri-

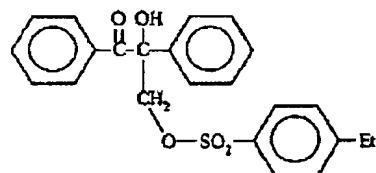
chloromethyl)-1,3,5-triazine. Exposure with an output of 1.0 W/cm<sup>2</sup> at an oxygen concentration of 15% by volume and a temperature of 140°C leads to tack-free, fully cured surface. In the scratch test the surface of the resin layer is permanently deformed starting from a load of 32 mN.

**Example 3:**

Experimental procedure as in Example 1. At a reduced oxygen concentration of 100 ppm and with the same light output the results obtained are like those in Example 1.

**Example 4:**

Experimental procedure as in Example 1. The light-activable curing agent used is a blocked sulphonic acid of the formula

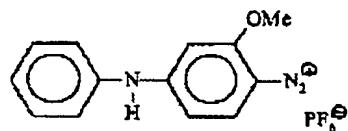


in a concentration of 1% by mass, based on the melamine resin.

The melt of the resin/curing agent mixture is applied with a layer thickness of 50 µm to a glass plate (thickness 6 mm) which has been heated to 140°C beforehand. Under irradiation conditions as in Example 1 a fully cured surface is obtained with an output of just 0.5 W/cm<sup>2</sup>. In the scratch test the surface of the resin layer is observed to undergo permanent deformation starting from a force of 30 mN.

**Example 5:**

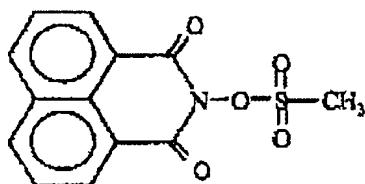
Experimental procedure as in Example 1; the light-activable curing agent used is a diazonium salt of the formula



in a concentration of 1% by mass, based on the melamine resin. A fully cured surface is obtained.

**Example 6:**

Experimental procedure as in Example 1; the light-activable curing agent used is a blocked sulphonic acid of the formula



in a concentration of 1% by mass, based on the melamine resin.

The melt of the resin/curing agent mixture is applied with a layer thickness of 50 µm to a glass plate (thickness 6 mm) which has been heated to 140°C beforehand. Under irradiation conditions as in Example 1 a fully cured surface is obtained.

**Example 7:**

The melamine resin used is a melamine-formaldehyde precondensate based on 2,4,6-trismethoxymethylamino-1,3,5-triazine and transesterified with an ethylene glycol diether of bisphenol A (Simulsol BPLE, Seppic S.A., France). The molar mass determined by GPC is 1800, the amount of unre-

acted Simulsol BPLE by HPLC analysis (solution in THF, UV detection with external standard) is 14% by mass. The fraction of the -OCH<sub>3</sub> groups in the transesterified melamine resin (determined by GC analysis following cleavage of the polytriazine ether with mineral acid) is 14.5% by mass. The viscosity at 140°C is 800 Pa.s.

The transesterification of the melamine-formaldehyde precondensate based on 2,4,6-trismethoxymethylamino-1,3,5-triazine and further condensation take place at 200°C in a GL 26 D44 laboratory extruder with vacuum devolatilizer (Leistritz) with a temperature profile of 100°C/130°C/130°C/200°C/200°C/200°C/200°C/200°C/200°C/100°C/100°C and an average residence time of 2 to 3 min. The extruder speed is 150 min<sup>-1</sup>. The intake zone of the extruder is fed gravimetrically through a side-stream feed with 2,4, 6-trismethoxymethylamino-1,3,5-triazine at 1.38 kg/h and with the ethylene glycol diether of bisphenol A at 1.13 kg/h. The strand of the polytriazine ether emerging from the extruder is chopped in a pelletizer.

The transesterified melamine resin is compounded at 130°C with 1% by mass, based on the melamine resin, of 2-(4-methoxyphenyl)-4,6-bis(trichloromethyl)-1,3,5-triazine as light-activable curing agent. The compound is melted in an extruder at a melt temperature of 150°C and is spun to filaments via a spinning pump and spinnerets at 145°C. The high-viscosity liquid melt filaments are irradiated at 135°C in the exposure unit with an output of 1 W/cm<sup>2</sup>. The fibres obtained in this way, which are 35 µm thick, can be wound up without sticking, whereas unexposed fibres very soon stick to one another.